INDUCTION OF FREEZING OF BULK SAMPLES OF SUPERCOOLED WATER BY PHYSICAL STIMULII.

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ABSTRACT.. Experimental results on the supercooling and induced nucleation of water as functions of air contents and dynamics are presented. Results represent unambiguous observation of the dynamically induced freezing of supercooled bulk water. The influences of the impurities on supercooling and nucleation are reflected on the normal freezing temperature of the particular sample. Average normal freezing temperature of $-6.8°C$ has been attained. Any deviation from the normal behaviour are attributed to the super-imposed factors. Nucleation could be triggered in the temperature range $-0.9°C$ to $-1.9°C$ by strong dynamics due to air bubbles. Ultrasonic waves could nucleate at $-5°C$ and $-3°C$ and $-3°5C$. Dagassed samples froze normally in the temperature range $-3.5°C$ to $-1.8°C$. Attempts have been made to explain the mechanism of supercooling and nucleation in terms of contaminations structure, energy balance and molecular Kinetics.

INTRODUCTION

Physical stimulii including (a) mechanical agitation, (b) acoustic waves, (c) shock waves, and (d) electric field have recently been gaining wide acceptance to investigate the freezing of supercooled water. Goyer *et al* (1965) have demonstrated that low intensity shock waves can trigger freezing of small samples of distilled water contained in glass and tygon tubings. References on the previous work may be found in the publications of Goyer *et al* (1965), Dorsey (1948), Van Hook (1961), Buckley (1951), Kapustin (1963), Shubnikov *et al* (1963), Chalmer (1964) and Matz (1954).

Freezing of water has been an intriguing problem since it was first pursued. Various theories on freezing of water, have been advanced so far but none of them as yet could satisfactorily explain the problem in question. Water has a definite, though changing, structure which depends on the orientation of the molecules with respect to one another and on the dissolved substances present. Further, it is well known from the investigations on ultrasonic absorption, x-ray diffraction, dielectric constants that about 30% of the water molecules in the liquid are arranged in a manner similar to that of ice. Phase transition and structural changes may be induced either by adding energy to or subtracting it from water.

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Water dissolves considerable amount of air at lower temperature. At —5°C and 1 atmosphere about 3.5 cc. air dissolves in 100 cc of water. The presence of air in the form of microbubbles is expected to have an appreciable control over the process of phase transformation of water. In the supercooled state, the dynamics of air bubbles would induce tiggering of nuleation. Mechanical agitation, sonic waves, shockwaves besides inducing nucleation are capable of releasing air trapped in water and thereby setting up of a dynamic state persisting even after the ceasation of inducing mechanism.

Literature on the systematic study of the dynamic nucleation of supercooled water is rare. The objectives of the present investigations will concentrate on the study of the following : (1) Energy distribution, (2) Molecular kinetics and (3) Structure of water, in connection with the understanding of supercooling and nucleation. The degree of supercooling attained gives an idea of the energy content, dynamics created by the movements of airbubbles generated in water sample determines the molecular kinetics and the process of nucleation involved suggests the structure of water. The basic principle underlying the actual structure is determined by the Gibbs free energy. The structure, which is thermodynamically the most stable, has the lowest free energy. At zero pressure and absolute zero temperature, a solid thus crystallizes in the structure with the lowest energy.

Supercooling of water depends on i) volumes, (ii) solid impurities present, iii) dissolved salts, iv) localized structure of water (aggregation of water molecules having the ice like structure), v) rate of energy abstraction, vi) dissolved gases and vii) interaction of external stimulii (ultrasonic waves, shock waves, mchanical agitations etc.)

For a given sample of water, the cumulative effects due to (i-vi) reflect on amount of supercooling attained. The temperature corresponding to nucleation determines the supercooling. The interaction of external stimulii with water so far supercooling and nucleation are concerned, is a complex one. Some time more supercooling is attained and some time instantaneous ceasation of further supercooling occurs.

Supercooling arises from the fact that more energy than available is required to fit the water molecules into the ice structure. A supercooled sample of water is metastable, since it will remain in the liquid state unless it is pushed over the energy barrier into the still more stable ice phase. The ice structure will persist there after as long as it remains at 0°C. The liquid to solid phase transition could be initiated at different levels of supercooling either by adding energy needed to overcome the energy barrier or by reducing the energy to such a level as required for a crystalline structure to form. The last process is affected by further cooling, thus slowing the motion of water molecules. The amount of work needed to assume the ice structure increases with the decrease of temperature because the viscosity of water almost doubles that at about 25°C. But a more sophisticated approach to the problem of supercooling, by fluctuation theory (Frankel, 1946) or by treating the early stages of formation of embyronic ice crystal as a quasi-chemical reaction between the water molecules shows that there will be always present a small number of embryonic ice crystals, and that nucleation may in principle always occur when the liquid is supercooled by the growth of these embryonic ice crystals. The suprcooled liquid is thus not metastable in the strict sense that it corresponds to a local, rather absolute, minimum of the availability ($A = U - T_0S + P_0U$), it is rather to be regarded as slowly transforming itself into the solid phase, but at so slow a rate as to be inappreciable.

Experiments (Blake, 1949; Galloway, 1953; Bhadra, 1961—1962; Leonard, 1950) on acoustically induced cavitation in gassy and degassed water, have demonstrated definitely that the tensile strength of degassed water is higher than that of gassy water. This means that the presence of gas (air) decreases the force of cohesion among the water molecules. Conversely speaking degassing or removal of air increase the strength of the force of cohesion i.e. the molecules are compacted to that extent as permissible by the existing thermal fluctuations. This suggests that degassed water would freeze at lower supercooling. The results of the present investigation justify the suggestion. In order to verify the ideas discussed in this section, a series of experiments have been performed. A detail representation of the experiments follows.

EXPERIMENT AND RESULTS

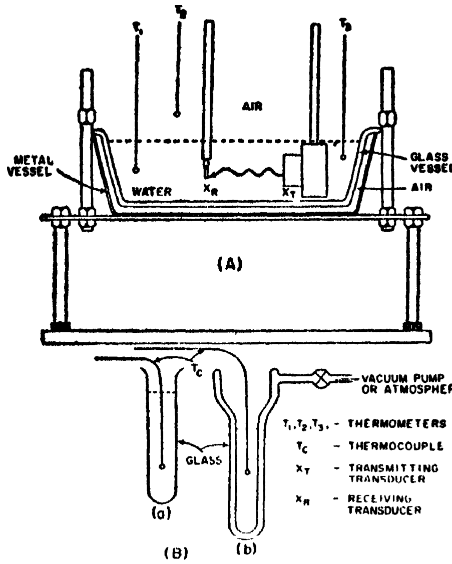
Four experimental set ups were devised to find out some of the answers to the problems on supercooling and induced nucleation of water, cited in the preceeding section. Bulk samples of water were investigated under various conditions. The principal features of the experimental conditions are summarized in table 1. The various types of apparatus developed are shown schematically in figure 1 and 2. The details of the shock tube have been published by Goyer *et al* (1965).

Set up I, Bulk water

Experimental arrangements are shown in figure 1A which is self explanatory. One litre of distilled water was taken in the glass vessel for investigation. T_x is the ultrasonic transmitting transducer and T_R, the detecting one. Thermometers T_1, T_2 registered the temperature of the sample of water and T_3 recorded the temperature of the surrounding air. The assembly was dipped into a bath cooled to -18°C. The sample of distilled water could be supercooled to $-3.5 \pm .4$°C.

(1) Samples of water, supercooled to about -1.0°C, were irradiated with short pulses (2-3 secs.) of ultrasonic energy at bout 1.0 Mc/s. The samples froze almost instantaneously at an average temperature of about -1.6°C.

(2) The sample of water when cooled to about $-2.5°C$ were stirred very gently with a thermometer. Freezing did not occur during agitation.



Fig, 1. Schematic diagram of the apparatus for supercooling bulk water

(3) Samples of water, supercooled to about $-2.5°C$ were stirred violently with a thermometer. Water froze instantaneously in the form of thin sheets throughout the whole mass. Ultrasonic irradiation and violent stirring with a thermometer of the sample produced air bubbles which subsequently grew in size and moved towards the water surface and escaped into the atmosphere.

Set up II

Samples of 16 to 20 cc. of distilled water were cooled in (1) an ordinary test tube and (2) a jacketted test tube. The inner dimensions of both tubes were the same. Both tubes, containing the same amount of distilled water and a thermocouple were dipped into the coolant at a temperature of about $-18°C$. Fig. 1B(a) and (b) show the schematics of the test tubes. The sample of water in the test tube fig. 1B(a) froze at about 0°C. A solid hard ice structure was formed on the walls and air bubbles collected along the axis of the test tube. The axial region appeared foggy. But the distilled water in the double jacketted test tube, fig. 1B(b) froze at $-6.0° \pm .4°C$ without any solid ice structure anywhere in the sample. Water crystallized in the form of thin sheets through the entire mass of the liquid.

Set up III

A new apparatus was designed to determine the effect of ultrasonics and gassing on the freezing of supercooled water. The modified apparatus permits the study of the effects of the growth and dynamics of air bubbles and of the air content. The schematic diagram of the apparatus is shown in figure 2. The glass portion of the apparatus consists of three coaxial tubes. The central tube holding the sample of water under investigation is sealed with an extra thin glass window (X in fig. 2) to insure the transmission of ultrasonic waves with negligible attenuation. A thermocouple probe is inserted into the water through a vacuum tight rubber stopper from the top of the tube which is also provided with a side tube for degassing. The second compartment, next to the central one contains air maintained at the desired pressure to control the cooling rate. The third one, i.e., the outermost one, is the cooling jacket.

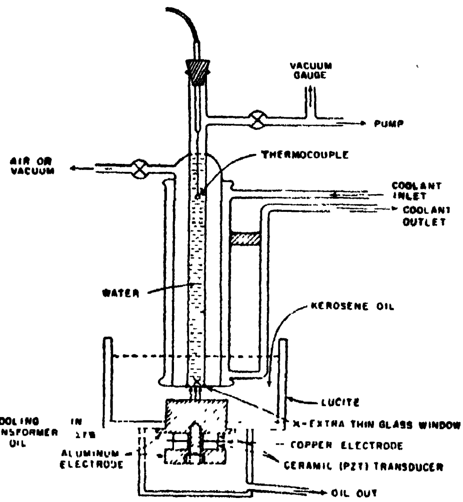


Fig. 2 Schematic diagram of the glass apparatus for supercooling water.

Ultrasonic waves were genrated at frequencies 128 to 130 kc/s in kerosene oil. In order to prevent cooling of the kerosene and insure optimum transmission of the ultrasonic energy, the sample of water was first cooled to the desired temperature and then the transducer head assembly was pushed up slowly so that the level of the kerosene, still at room temperature, just covered the lower part of the glass apparatus containing the sample under investigation. Ultrasonic wave transmission through the sample was detected visually by the growth and the movement of air bubbles and the bulging out of the water surface.

The ambient pressure on the water surface was reduced by means of a water pump. The measured pressure of the air in water was 1mm. Hg which was estimated by determining the equilibrium vapour pressure on the surface of the sample of water at that temperature. At the start of evacuation a large number of air bubbles were generated throughout the bulk of the water and because of the pressure gradient constituted a dynamic system in the medium. Degassing was started at different stages of cooling. Experiments were repeated several times to obtain average values of the temperature of freezing of water under different experimental conditions.

The natural freezing temperature of 16c.c. distilled water contained in the triple jacketted glass vessel ranged from $-5.0°C$ to $-7.0°C$ having the average of $-6.8°C$.

(1,2) Ultrasonic waves at frequencies ranging from 125 to 130 Kc/s triggered freezing of supercooled sample almost instantaneously at $-5.0°\pm.2°C$ and $-3.5°\pm.4°C$.

(3) Samples of 16 cc. distilled water, of average natural freezing temperatures $-6.5°\pm.4°C$ froze at temperatures ranging from $-0.9°$ to $-1.9°C$ when the degassing of samples was started at about $0°C$.

(4) Samples of 16 cc. water froze at temperatures ranging from $-5.5°C$ to $-6.5°C$, when simultaneous cooling and degassing were started at room temperature (20 to 22°C).

(5) Samples of 16cc. water degassed and kept under atmospheric pressure overnight, froze at $-3.5°\pm.2°C$, $-2.8°\pm.2°C$ and $-1.8°\pm.2°C$. These samples, when allowed to freeze a second time without repeating the process of degassing froze at $-4.0°\pm.2°C$, $-3.8°\pm.2°C$ and $-3.8°\pm.2°C$.

(6) Samples of 16 cc. water degassed and kept under reduced pressure overnight froze at $-5.8°C$, $-6.3°C$, and $-5.8°C$ corresponding to the range of temperatures for natural freezing of the same volume of water.

DISCUSSIONS

All the experiments described in the preceding section were planned to study how (i) contamination, (ii) energy content (iii) kinetics and (iv) local structure of water, affect supercoolling and nucleation of bulk samples of water. Supercooling depends on the ratio of cooling. At rapid rate of cooling samples froze at about 0°C whereas at low rate of cooling, the samples could be cooled much lower than 0°C. This is evident from the results obtained in experiments set up II.

In order to meet the experimental exigencies apparatus described in setup III were designed so the discussion on the above mentioned points will be based primarily on the results obtained in set up III for bulk samples.

Under a particular environmntal condition, the natural freezing temperatures of each of the samples were determined first by repeating several times. Natural freezing temperature is taken to be that temperature at which the sample froze due to the slow process transference of heat to the environment. Much attention was paid to determine the range of variation of natural freezing temperature because any deviation from the normal range of temperature would indicate the effect due to the imposed conditions. The effects due to different types of conta-

Table 1

Summary of the experimental conditions to determine the freezing temperature of bulk water

Experiments	Se. No.	Apparatus used	Quantity of water	Temp. of the cooling bath	Physical stimuli applied at temperature and conditions	Characteristics of external agents to induce freezing
Set up I	1	Fig. 1A	one litre	$-18°C$	$-1°C$	1 Mc/s ultrasonic energy lasting for (2-3) sec.
	2	”	”	”	$-2.5°C$	—Slow stirring.
	3	”	”	”	$-2.5°C$	—Violent agitation.
Set up II	1	Fig. 1B(a)	(16-20) c.c.	”	22°C	Rapid cooling.
	2	Fig. 1B(b)	”	”	22°C	Slow cooling.
Set up III	1	Fig. 2.	16 c.c.	”	$-5°C$	(125-130) Kc/s ultrasonic energy.
	2	”	”	”	$-3°.5°C$	”
	3	”	”	”	0°C	On set of degassing.
	4	”	”	”	(20-22)°C	Simultaneous cooling and degassing.
	5	”	”	”	Degassed and kept at latm overnight.	Slow cooling.
	6	”	”	”	Degassed and kept under reduced pressure overnight.	”

minations were not considered separately. The cummulative effects reflected on the natural freezing temperatures which served as control for subsequent experiments. In the present investigation air was tagged as a contamination; energy was supplied from external sources either by ultrasonic waves or by creating dynamics in the samples and the degree of supercooling attained indicated the local structure of the samples.

The results obtained in these two sets of experiments are summarized in table 2 for bulk samples. In these experiments the growth and the movements of air bubbles were initiated by ultrasonic waves of 125-130 Kc/s and by pumping out the air occluded in the supercooled water. Table 2, column 2, shows the range (−5.7°C to −7.0°C) as the normal freezing temperature of 16 cc samples of water. Degassed samples were allowed to settle done in overnight time under 1 atmosphere pressure. The freezing temperatures of these samples ranged between −3.5°C and −1.8°C. In a subsequent run with these samples without repeating the process of degassing, nucleation occurred at −4.0°C, −3.8°C and − 3.8°C as shown in table 2 column 6. This range of freezing temperatures is much higher than the natural freezing temperatures of the normal samples. The results indicate positively the influence of the air content on the freezing temperature of water. After degassing, the samples were opened to the atmosphere. The degassed samples of water at partial air pressure of 1 mm. Hg, were pressurized by exposing them to atmosphere. It is well known that without collision, free molecular diffusion does not occur immediately. The consequence of pressurization leads to an increase in the force of attraction between the molecules, i.e., the molecules were brought closer together and as a result the samples froze at temperatures warmer than they would naturally freeze. The results are shown in table 2, column 6.

The samples of degassed water kept under reduced pressure overnight froze at −5.8°C, −6.3°C, and −5.8°C, as shown in column 7. This temperature range corresponds almost to that of natural freezing as shown in table 2, column 2. The dissolved air was partially removed from the samples which were then allowed to settle down overnight under reduced pressure; the samples did not freeze at higher temperatures as occurred in the previous cases where the samples were degassed and exposed to the atmosphere overnight (column 6). In this instance, the situation is different. Under reduced pressure, the rate of evaporation of water is increased due to the lowering of the boiling point. Consequently, the molecules have a greater tendency to move apart from each other and the forces of attraction among the molecules are decreased. Consequently, the molecules are unable to come closer together to assume the ice structure until the internal energy of the system is reduced. This interpretation holds good also for the results shown in column 5 because the experimental procedures involved in both cases were very nearly the same.

The samples of bulk water froze at temperatures ranging from 0.9°C to −1.9°C as shown in table 2, column 4, when the degassing of the samples was started at about 0°C. The degassing, performed with the pump, produced a considerable number of air bubbles throughout the entire volume of water. As they moved towards the lower pressure region, that is, the surface of the liquid, they grew and ultimately escaped into the atmosphere. The growth and the movement of the air bubbles introduced a dynamical system in the water medium. The probability of energy transfer between water-water and water-air molecules was increased by the dynamics of the air bubbles and as a result, water molecules in the metastable state attained the right amount of energy to assume the ice structure. The degassing was started at about 0°C, so that a sufficient amount of air would remain in the water by the time the temperature dropped below 0°C. This is an essential condition of the experiment to insure the required energy transfer between water-water and water-air molecules during the process of the growth and motion of the air bubbles.

Consequently, the freezing occurs at warmer temperatures, i.e., one or two degrees below 0°C. On the other hand, the samples do not freeze at warmer temperatures if an insufficient amount of air is left in the water to produce the dynamics befitting freezing of the samples as shown in table 2, column 5. Here the samples were subjected to simultaneous cooling and degassing. By the time the samples were cooled to 0°C, practically no air bubbles were visible in the water and consequently the dynamics of air bubbles could not play any part in the process of freezing. The samples froze, at −5.5°C, −6.5°C and −6.5°C, i.e., at the natural freezing temperatures as shown in column 2 of the table. The results shown in column 5, and the results shown in Column 7 are within the same limited range. The results in column 5 of the table indicate the air bubbles are essential to the triggering of induced freezing of the samples of water. The results presented in columns 4 and 5 and in columns 2 and 6 of table 2 indicate the pronounced effect of (i) the dynamics of air bubbles and (ii) the air content, respectively, on the freezing of bulk water. The results presented in columns 6 and 7 show that the criterion for initiating freezing at warmer temperatures (1° or 2° below 0°C) is not only the removal of the dissolved air but also the compacting of the water molecules into the tighter lattice and further it indicates that dynamics created more embyronic ice to form the nucleus for initiation of freezing.

The results of the effect of ultrasonic waves on the freezing of bulk water are shown in Column 3 of the table. A large number of air bubles were generated within the sample of water by the ultrasonic energy at frequencies of 125-130 Kc/s. These bubbles moved towards the surface of the water and escaped to the atmosphere. The samples froze at −5.0°C and −3.5°C after three to five seconds of irradiation. The interaction of ultrasonic energy with liquid is very complex. Turner and Van Hook (1956), reported that low frequency (8-16 Kc/s) and high

Table 2

Freezing of distilled water contained in triple jacketted glass vessel Freezing temperature in —°C

	1	2	3	4	5	6	7
Sl. No.	Volume in cc	Natural	Sonic Wave	Delayed Pumping out of Air (near 0°C)	Simultaneous Cooling and Pumping Started At Room Temp.	Degassed Then Kept Open to Atmosphere Overnight	Degassed But Kept Under Reduced Pressure Overnight
1.	20	6.0					
2.	18	6.0					
3.	,,	6.2					
4.	,,	5.0					
5.	,,	5.8					
6.	,,	7.0					
7.	,,	6.2					
8.	,,	6.0					
9.(a)	,,	6.0					
(b)	,,		5.0				
(c)	,,		3.5				
10.(a)	16	6.5					
(b)	,,			1.0			
11.(a)	,,					3.5	
(b)	,,					4.0	
12.	,,			0.9			
13.	,,					2.0	
14.(a)	,,	6.2					
(b)	,,				5.5		
15.(a)	,,					2.8	
(b)	,,					3.8	
16.	,,				6.5		
17.	,,						5.8
18.	,,						6.3
19.(a)	,,					1.8	
(b)	,,					3.8	
20.	,,			1.2			
21.	,,					1.8	
22.(a)	,,	5.7					
(b)	,,				6.5		
23.	,,						5.8
24.	,,			1.8			
25.	,,			1.9			
26.	,,					3.2	

Numerical figures indicate experiments in chronological order with fresh samples ofwater. Alphabetical figures indicate that the same sample of water was used in that numerical sequence.

power (2 sonic watts) caused immediate ice formation when distilled water was supercooled by 1 or 2°C. High frequency ultrasonic waves (340 Kc/s) failed trigger freezing but delayed it. Ives (1951) observed that any violent, non-uniform noise or sound could trigger freezing of supercooled fog droplets, in agreement with the observations of Maurin and Medard (1947) and recent field observations by Goyer (1965). Alport (1956) discussed these effects suggesting the possibility of seeding supercooled clouds in the temperature range where silver iodide and naturally occurring nuclei are ineffective . The mechanism of the interaction of acoustic waves and supercooled liquids in phase transition is not yet clearly understood. In this case only the evolution of air bubbles by ultrasonic energy is considered. Ultrasonics have been proved to be the best device for degassing liquid (Galloway, 1953; Bhadra, 1961). Low intensity ultrasonics is used for degassing whereas high intensity ultrasonics is used for determining the threshold for cavitation. Degassing and Cavitation are two distinct processes having specific characteristics. While degassing air bubbles are generated, the the mechanism involved for the energy transfer may be explained in the following way. An air bubble is much more compressible than the surrounding water, it pulsates with a large amplitude when exposed to the pressure variation in a sound field. To follow the pulsation of the bubble, the water immediately surrounding the bubble must oscillate with an amplitude larger than that of water at a larger distance from the bubble. The mass of the surrounding water, coupled with the compressibility of the air in the bubble, results in a resonance at a frequency that is determined by the diameter of the bubble and the pressure of the air in the bubble. The large amplitude vibrations of air bubbles thus transfer requisite energy for the affected molecules to form the ice structure.

The results of the present investigations arrive at the following conclusions :

(1) Nucleation could be induced in bulk water by creating strong dynamics of air bubbles inside the sample.

(2) In the absence of airdynamics, induced nucleation could not be produced. (In a private communication, Dr. G. G. Goyer of NCAR, Boulder, colorado confirmed this observation by performing experiments with high speed photographic technique).

(3) Removal air from samples of water produced lower degree of supercooling whereas aeration produced higher supercooling.

Higher supercooling indicates insufficient number of water molecules having the ice structure as required to initiate nucleation.

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